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Specular X-Ray Reflectivity from Photonically Functionalized Siloxane-Based Calix[4]arenes Scaffolds on Transparent Surfaces

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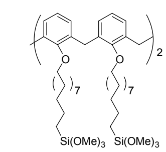
Beamline(s): X23B

Introduction: The design and development of new molecule-based photonic materials with excellent optical, thermal, and chemical properties is a topic of much current interest [1]. Most challenging is the development of covalently immobilized chromophores/fluorophores to prepare novel photonically robust molecular arrays directly on silicon or related substrates allowing facile device integration. We report the X-ray reflectivity study of the formation and characterization of molecular precise siloxane-based monolayers based on photonic bifunctionalized calix[4]arene molecular scaffolds.

Methods and Materials: Synthesis of photonically functionalized calix[4]arene molecular scaffolds and the formation and characterization of self-assembled monolayers (SAMs) is described in [2]. Two identical chromophores were covalently attached to the upper rim of the bifunctional template calix[4]arene (at the 1 and 3 positions), whereas the lower rim was functionalized with four reactive silane groups to ensure strong, covalent multidentate binding to various hydrophilic surfaces (e.g., quartz, silicon). Various homo- and heterogeneous nanoscale thin films (1.2-2.1 nm thick) were assembled from solution and synchrotron specular x-ray reflectivity (XRR) was used to quantitatively determinate the microstructure of these new photonic molecular materials.

Results: Fig. 1b shows normalized reflectivity data (R/R_F) from **3**, **8**-based and from the mixed **3**,**12**-based films (Fig. 1a). Solid lines in Fig. 1 show best fits assuming an uniform electron density film with error-function-broadened interfaces (see, for example, [3]). The XRR measurements on **3** and **8**-based monolayers reveal (i) a film thickness of 12.1 ± 0.5 Å (**3**) and 18.3 ± 0.7Å (**8**), (ii) a film-air roughness of ~6.9 Å (**3**) and ~6.0 Å (**8**) and a film-substrate roughness of ~4.6 Å (**3**) and ~4.0 Å (**8**), respectively, and (iii) a molecular surface density of 140 ± 10 Å^2/molecule (7.1 × 10^{13} molecules/cm^2) (**3**) and 220 ± 10 Å^2/molecule (4.5 × 10^{13} molecules/cm^2) (**8**). XRR analysis in combination with MM$^+$ calculations indicate an average molecular tilt angle of ~45º (**3**) and ~50° (**8**) from the surface normal. The mixed **3**,**12**-based films have two regions. The first region, the calix[4]arene layer **3**, has a thickness of 12.0 Å and an electron density of ρ = 0.40 electrons/Å^3. The second region, the chromophore layer, has a thickness of 8.6 Å and ρ ~ 0.30 electrons/Å^3. The interfacial and surfaces roughness, ~1.4 Å and ~2.8 Å, respectively, are less than the Si(111) substrate roughness (~4.5 Å). The film is remarkable smooth considering the fact that it consists of two bulky components (**3**, **12**) with entirely different molecular dimensions. The "molecular footprints" for the two regions, ~140 Å^2/molecule and ~310 Å^2/molecule indicate that the ratio between **3**:**12** = 1:0.8 on the surface. The average XRR-derived film roughness and surface densities of **3**, **8** and the mixed **3**,**12**-based SAMs are comparable arguing that the overall film structure is largely dictated by the calix[4]arene template and not by the chromophores.



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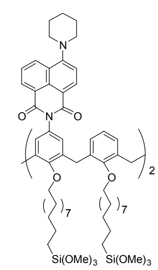

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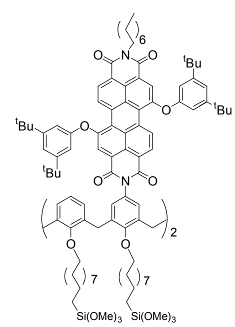

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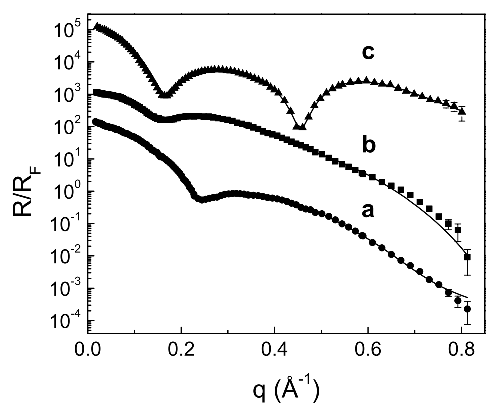

Figure 1. a) Schematic representation of the photonically functionalized siloxane-based calix[4]arenes scaffolds (**3**, **8**, and **12**); b) XRR data for the **3**- (a), **8**- (b) and the mixed **3**,**12**-based (c) monolayers. The data is shifted vertically for clarity. The solid lines are the best fits to the experimental data.

Conclusions: XRR measurements show the formation of structurally regular, highly dense organic films. Functionalization of the calix[4]arene upper rim at the 1 and 3 position with two dyes might drastically alter its spectroscopic properties due to intramolecular chromophore-chromophore interactions. The presented results argue that this calix[4]arene templated assembly method may be suitable for a wide range of chromophores.

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References: [1] A.S. Lukas, M.R. Wasielewski, Molecular Switches, Ed. Feringa, B. L. Wiley-VCH GmbH, Weinheim, Germany, 2001, pp. 1-35 ; [2] T. van der Boom et al, Langmuir, submitted; [3] G. Evmenenko et al., J. Chem. Phys. **115**, 6722 (2001).